Glycerol reforming and methanol synthesis for the production of renewable methanol

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Summary

Biodiesel production has grown exponentially in the first decade of the 21th century. During the production process about 10 kg of glycerol is formed for every 100 kg of biodiesel. As a consequence, the development of alternative product outlets for glycerol is high on the research agenda of companies and research institutes. One of the attractive opportunities is the production of green methanol from glycerol, which can be reused in the biodiesel production process. This option has been actively explored within the European Supermethanol project. The goal of this project is to develop a blueprint for a process to convert glycerol into methanol which can be implemented and integrated in an existing biodiesel plant. In this dissertation, the research activities on methanol production from glycerol within the scope of the Supermetha-nol project are described.

The envisaged Glycerol-to-Methanol (GtM) process consists of a glycerol reforming step in supercritical water to syngas with subsequent methanol synthesis (**Chapter 1**). In the reforming step in supercritical water, a syngas at high pressure (> 20 MPa) is obtained. High pressures are attractive with respect to the chemical equilibria in methanol synthesis. In combination with a relatively low temperature (473 – 523 K), high equilibrium conversions are attainable. The research described in this dissertation focuses on optimizing the reforming of glycerol in supercritical water and high pressure methanol synthesis addressing among others the influence of process conditions. Finally, the two processes are integrated for a unique experimental demonstration of the GtM-process aiming at high methanol yields.

Glycerol reforming in supercritical water, produces a gas mixture containing H_2, CO, CO_2, CH_4, and higher hydrocarbons (C_2H_4, C_2H_6, C_3H_6, and C_3H_8). The gas composition is a strong function of the operating conditions and the presence of a catalyst (**Chapter 2**). For noncatalytic reforming and reforming in the presence of alkali salts, the gas composition is a function of the glycerol conversion and, besides initial glycerol decomposition reactions, the water-gas shift reaction plays a major role. H_2, CO, CH_4, and at least the olefins are primary gas phase products, while the other components are formed in subsequent gas phase reactions. Complete conversion of 1 mole glycerol yields roughly 2 moles of carbon oxide (CO and CO_2) and 1 mole of hydrocarbon.

Unfortunately, this gas composition is not very attractive for methanol synthesis as the hydrocarbon content is rather high (max. ±20 vol%). To reduce the hydrocarbon content, catalytic reforming with dedicated catalysts was investigated (**Chapter 3**). Five different catalysts were tested, with different active metals. All catalysts were found to promote the water-gas shift reaction over the complete temperature range, and for four out of five catalysts almost all CO was converted to CO_2. Catalysts containing Ni demonstrated both beneficial and adverse properties. All higher hydrocarbons were reformed, but the CH_4 concentration approached equilibrium for temperatures exceeding 750 K. Low CH_4 concentrations could only be obtained by the combination of high temperature and low feed concentrations.

In preliminary methanol synthesis experiments, the *in situ* formation of liquid methanol was demonstrated visually in a high pressure view cell reactor (**Chapter 4**). *In situ* condensation

of liquid has never before been demonstrated directly, and this phenomenon has very important consequences for the equilibria in methanol synthesis. As the products (methanol and water) are partly withdrawn from the gas phase, the limitations imposed by the chemical equilibria are almost completely eliminated. To obtain insight into the (positive) influences of condensation on the equilibria, an equilibrium model was developed accounting for the formation of a liquid phase (**Chapter 5**). The experimental data showed excellent correlation with the model predictions, in particular at the lower temperatures (468 – 523 K). At operating temperatures around 473 K and a pressure of 20 MPa, unprecedented experimental conversions up to 99.5% of the limiting components were obtained in a packed bed reactor. Operation at these high conversion levels has major benefits for methanol synthesis, and for instance eliminates the syngas recycle stream, which is typically used in conventional methanol synthesis.

High pressure methanol synthesis has been investigated experimentally for several syngas compositions ranging from gases typically used in commercial methanol synthesis to gases obtained in the reforming of glycerol in supercritical water (**Chapter 6**). For all types of gas, high conversions were observed when using a conventional methanol synthesis catalyst (Cs doped $Cu/ZnO/Al_2O_3$). When CO_2 is the major carbon oxide in the gas, the purity of the organic fraction exceeded 99.9%. Gases with higher CO content lead to the formation of substantial amounts of higher alcohols (max. 13 vol%). Furthermore, methanol production rates have been measured in a stirred basket reactor. The experimental data were modeled using a standard kinetic expression for heterogeneous catalysts, and a kinetic equation (the first in its sort) for methanol synthesis at high pressure and low temperature was derived (**Appendix C**).

Finally, the GtM-process was demonstrated experimentally in a dedicated continuous bench scale unit with 1 kg/h aqueous feed (**Chapter 7**). Glycerol reforming and methanol synthesis were integrated and experiments were performed to maximize the conversion of carbon in glycerol to carbon in methanol. The best results were obtained when glycerol was reformed at 998 K using a methanation catalyst (Ni as active metal) in the reforming section. The gas consisted of mainly H_2 and CO_2 while CH_4 levels remained below 2.4 vol%. Subsequently, the gas was converted to methanol in three packed bed reactors in series with a decreasing operating temperature (513 – 481 K). The maximum methanol yield was 0.62 kg methanol/kg glycerol. This is no less than 76% of the maximum theoretical yield of 0.81 kg methanol/kg glycerol.

A conceptual design was prepared by Uhde, Germany for a commercial GtM-process. In the current situation (2012), subsidies for renewable methanol are required to make this process profitable (**Chapter 8**).

The work performed has been of great value in quantifying the potential for the conversion of glycerol by reforming in supercritical water, combined with high pressure methanol synthesis. It identifies key phenomena, experimental results, and conclusions which may provide a firm basis, or simply inspiration for others who are drawn to this field of investigation.